

# HIGH DURABILITY STRUCTURES OF AMORPHOUS ALLOY AND A METHOD OF FORMING

## FIELD OF THE INVENTION

The present invention relates to articles of bulk-solidifying amorphous alloys with improved durability and fatigue life, and to methods of improving durability and fatigue life of bulk-solidifying amorphous alloys.

## BACKGROUND OF THE INVENTION

Amorphous alloys (or metallic glasses) have no discernable pattern existing in their atomic structure in contrast to ordinary crystalline metals and alloys. This unique atomic structure results in very high yield strengths and high hardnesses for amorphous alloys. These superior properties are generally attributed to the lack of the dislocations typically found in crystalline atomic structures. In addition, amorphous alloys generally have high elastic strain limits approaching, up to 2.0 %, much higher than any other metallic alloys. For example, the yield strength of Ti-base amorphous alloys is about 2 GPa or more, values exceeding the current state of crystalline titanium alloys. Finally, amorphous alloys can be formed by a variety of methods among which quenching from the liquid state is the most common and widely used method.

However, amorphous alloys in bulk forms (alloys capable of being formed with a minimum dimension of at least 0.5 mm, which are also referred to as bulk-solidifying amorphous alloys or bulk amorphous alloys) have some shortcomings which result in reduced utilization of the high yield strength and high elastic strain limit properties of these materials in load bearing structural applications. First, the sensitivity of amorphous alloys to defects and their low resistance to crack propagation from defects are primary causes of premature failure. For example, the fatigue endurance limit of amorphous alloys can be quite low, and values as low as 10 % of its ultimate strength have been reported. In the case of high stress-low cycle cases, amorphous alloys generally fail around 50 % of their ultimate strength after several thousands cycles. This is generally attributed to the “micro-structureless” nature of the amorphous phase and the lack of any of the work-hardening mechanisms typically found in crystalline alloys.

Accordingly, the conventional work hardening and strengthening methods generally used for crystalline alloys have been deemed to be non-applicable to amorphous alloys. Therefore, some composite forms of amorphous alloys have been developed to remedy the shortcomings of toughness and fatigue resistance. Although these composites show improvement in the toughness and durability (or fatigue resistance) it can only be done at the expense of the high yield strengths and the high elastic strain limits of the pure amorphous alloy materials, and as such defeat the principal benefits of using these materials.

1 Accordingly, there is a need for amorphous alloys with improved durability and fatigue resistance that are capable of maintaining relatively high yield strengths and high elastic limits in loading bearing structural applications.

5 **SUMMARY OF THE INVENTION**

The current invention is directed to articles of bulk-solidifying amorphous alloys with improved durability and fatigue life, and more specifically to articles of bulk-solidifying amorphous alloys subjected to a surface treatment utilizing a shot-peening process.

10 The invention also relates to methods of improving the durability and fatigue life of bulk-solidifying amorphous alloys utilizing a shot-peening process.

In one embodiment of the invention, the shot-peening process is applied to cover a substantial portion of the surface of an amorphous alloy article.

15 In another embodiment of the invention, the shot-peening process is applied to at least the portion of the surface of the amorphous alloy article with the maximum tensile stresses.

20 In still another embodiment, the invention is an article of amorphous alloy where at least a portion of the surface is subjected a shot-peening process.

In yet another embodiment, the invention is an article of an in-situ amorphous alloy composite and at least a portion of the surface of the article is subjected to a shot-peening process.

25 In still yet another embodiment, the invention is a golf club face insert made of an amorphous alloy or an in-situ amorphous alloy composite, and the back surface of the insert is treated with a shot-peening process.

**DETAILED DESCRIPTION OF THE INVENTION**

30 The current invention is directed to articles of bulk-solidifying amorphous alloys with improved toughness, durability and fatigue life, and more specifically to articles of bulk-solidifying amorphous alloys subjected to a surface treatment utilizing a shot-peening process. The invention is also directed to methods of improving the toughness, durability and fatigue life of bulk-solidifying amorphous alloys utilizing a shot-peening process.

35 Shot-peening is a means of cold working the surface of metal parts by means of a hail or blast of round metal shot directed against the surface. Although other metal shots can be used, round shots made of heat-treated steel are generally satisfactory for use. The hardness of the metal shot is generally in the range of from 45 Rc to 60 Rc, or more. The diameter of the round shot size is generally in the range of 0.003" to 0.20" or more. Preferably the metal shot size is in the range of 0.006" to 0.040".

35 The inventors have found surprisingly that the toughness and durability of bulk amorphous alloys can be dramatically improved by shot-peening the surface, a process which is generally reserved for metals, which exhibit both work hardening and with ductility.

1 Surprisingly, the shot-peening process can be used to alleviate the effects of various defects  
on the amorphous alloys despite the limited ductility of amorphous alloys and the difficulty  
of cold-forming these materials.

5 Although any suitable amorphous alloy may be used with the current invention, a  
particularly preferred set of amorphous alloys are "bulk solidifying amorphous alloys". Bulk  
solidifying amorphous alloys are recently discovered family of amorphous alloys, which can  
be cooled at cooling rates of about 1,000 K/sec or less, substantially lower than traditional  
10 amorphous alloys, and retain their amorphous atomic structure. As such, these bulk  
solidifying amorphous alloys can be produced in thicknesses of about 0.5 mm or more,  
substantially thicker than conventional amorphous alloys which have maximum thicknesses  
15 of about 0.020 mm, and which require cooling rates of  $10^5$  K/sec or more. U.S. Patent Nos.  
5,288,344; 5,368,659; 5,618,359; and 5,735,975, the disclosures of which are incorporated by  
reference in their entirety, disclose such bulk solidifying amorphous alloys.

15 One exemplary family of bulk solidifying amorphous alloys can be described as  
 $(Zr,Ti)_a(Ni,Cu,Fe)_b(Be,Al,Si,B)_c$ , where a is in the range of from 40 to 75, b is in the range  
of from 5 to 60, and c in the range of from 0 to 40 in atomic percentages. Furthermore, these  
alloys can accommodate substantial amounts of other transition metals up to 20 % atomic  
percentage, and more, including preferably metals such as Nb, Ta, V, and Co.

20 A preferable alloy family is  $(Zr,Ti)_a(Ni,Cu)_b(Be)_c$ , where a is in the range of from 40  
to 75, b is in the range of from 5 to 50, and c in the range of from 5 to 40 in atomic  
percentages. Another preferable alloy family is  $(Zr)_a(Nb,Ti)_b(Ni,Cu)_c(Al)_d$ , where a is in the  
range of from 45 to 65, b is in the range of from 0 to 10, c is in the range of from 20 to 40,  
25 and d in the range of from 7.5 to 15 in atomic percentages. In these alloys, Zr can be  
substantially substituted by Hf and other elements such as Cr, V, Ta, Mo, and W can also be  
added in limited amounts.

30 Another set of bulk-solidifying amorphous alloys are based on ferrous metals (Fe, Ni,  
Co). Examples of such compositions are disclosed in U.S. Patent No. 6,325,868, and in  
publications to (A. Inoue et. al., Appl. Phys. Lett., Volume 71, p 464 (1997)), (Shen et. al.,  
Mater. Trans., JIM, Volume 42, p 2136 (2001)), and Japanese patent application 2000126277  
(Publ. # 2001303218 A), the disclosures of which are incorporated herein by reference. One  
35 exemplary composition of such alloys is Fe72Al7Zr10Mo5W2B15. Although, these alloy  
compositions are not as processable as the Zr-base alloy systems, they can be still be  
processed in thicknesses of around 1.0 mm or more, sufficient enough to be utilized in the  
current invention. In these alloys, high atomic number elements as Ta, Nb, Mo, Zr, and W  
can also be used as alloying additions to increase radiation shielding effectiveness.

In general, crystalline precipitates in bulk amorphous alloys can be highly detrimental  
to their properties, especially to the toughness and strength of these materials, and as such it  
is generally preferred to minimize the volume fraction of these precipitates if possible.

1 However, there are cases in which ductile crystalline phases precipitate in-situ during the  
processing of bulk amorphous alloys, which can be indeed beneficial to the properties of bulk  
amorphous alloys, and especially to the toughness and ductility of these materials. Such bulk  
5 amorphous alloys comprising such beneficial precipitates are also included in the current  
invention. One exemplary case is disclosed in (C.C. Hays et. al, Physical Review Letters,  
Vol. 84, p 2901, 2000), the disclosure of which is incorporated herein by reference.

10 In one embodiment, the shot-peening is applied to at least a portion of an amorphous  
alloy article. In another embodiment, the shot-peening is applied to cover a substantial  
portion of the surface of the amorphous alloy article. In one preferred embodiment, the shot-  
peening is applied to cover substantially the entire surface of the article, which is subjected to  
15 tensile stresses in service. For example, in the case of a rotating round beam, such as a  
transmission shaft, where the surface is subjected to maximum tensile stresses even  
momentarily, the shot-peening is applied to the whole circumferential surface of the rotating  
round beam. In another embodiment, the shot-peening is applied to at least a portion of the  
20 surface of an amorphous alloy article with the maximum tensile stresses. For example, in the  
case of an article subject to bending in one direction, the shot-peening is applied to the  
surface on the opposite side of the loading (e.g. to the backside of a face of a golf club). In  
one embodiment, the article is a golf club face insert made of amorphous alloy or an in-situ  
amorphous alloy composite, and the back surface of the insert is treated with shot-peening  
process.

The following examples illustrate representative applications of the current invention,  
but do not limit the scope of how the current invention can be beneficially used in other  
applications:

25 **EXAMPLE 1:**

30 Three samples of an untreated golf club face insert made of a bulk-solidifying  
amorphous alloy (VIT-001 trade designation Zr (41.2) Ti(13.8) Cu (12.5) Ni(10) Be (22.5)  
atomic percent) were loaded to a failure with loading applied on the front hitting surface. The  
samples failed with peak loads varying from 2,300 lbs to 2,700 lbs. The back side of similar  
samples from the same lot were subjected to a shot-peening process with nominal Almen  
Intensity (a standard measuring procedure to calibrate the intensity of shot-peening process)  
of .0085A and shot size of S230R (0.023" shot diameter). The samples were then subjected to  
the same loading conditions and failed with peak loads of over 3,300 lbs.

35 **EXAMPLE 2:**

The untreated golf club face insert samples of Example 1 were subjected to a fatigue  
cycling loading (similar to in example 1) with a peak load of 2,100 lbs and a minimum load  
of 1/10 of peak load. The samples failed after several hundreds cycles (between  
approximately 200 cycles to 900 cycles). The back side of similar samples from the same lot

1        were subjected to a shot-peening process with nominal Almen intensity of ,0085A and shot size of S230R (0.023" shot diameter). The samples were then subjected to the same fatigue cycling loading conditions, and survived more than 3,000 cycles.

5        EXAMPLE 3:

      The back side of untreated golf club face insert samples of Example 1 were subjected to a shot-peening process with nominal Almen intensity of ,0060A and shot size of S230R (0.023" shot diameter). The samples were then subjected to the same fatigue cycling and a peak load of 2,400lbs. The treated samples survived more than 3,000 cycles.

10      EXAMPLE 4:

      The back side of untreated golf club face insert samples of Example 1 were subjected to a shot-peening process with nominal Almen intensity of ,011A and shot size of S330R (0.033" shot diameter). The samples were then subjected to the same fatigue cycling and a peak load of 2,700 lbs. The treated samples survived more than 1,400 cycles.

15      EXAMPLE 5:

      Three samples of untreated golf club face inserts made of a bulk-solidifying amorphous alloy in-situ composite with dendritic beta phase (LM-2 trade designation Zr (56.2) Ti(11.2) Nb (7.5) Cu (6.9) Ni(5.5) Be (12.5) atomic percent) were subjected to a fatigue cycling with a peak load of 2,400 lbs applied on the front hitting surface. The samples failed after several hundreds cycles (between approximately 200 cycles to 500 cycles). The back side of similar samples from the same lot were subjected to a shot-peening process with nominal Almen intensity of ,006A and shot size of S230R (0.023" shot diameter). The samples were then subjected to the same fatigue cycling and loading conditions, and survived more than 1,500 cycles. Another set of similar samples were subjected to a shot-peening process with nominal Almen intensity of ,006A and shot size of S330R (0.033" shot diameter). The samples were then subjected to the same fatigue cycling and loading conditions, and survived more than 3,000 cycles.

      In addition to the specific features and embodiments described above, it is understood that the present invention includes all equivalents to the structures and features described herein, and is not to be limited to the disclosed embodiments. For example, the effects of shot-peening on the surface of the amorphous alloys can be achieved through other suitable, alternative means such as laser shock peening, wherein the stress is introduced by a shock wave generated by instantaneous ablation of a small amount of material on the surface when a high intensity laser beam illuminates the surface. The same flexibility for practicing the invention is true with respect to the particular amorphous alloy selected. Accordingly, individuals skilled in the art to which the present articles and methods pertain will understand that variations and modifications to the embodiments described can be used beneficially without departing from the scope of the invention.